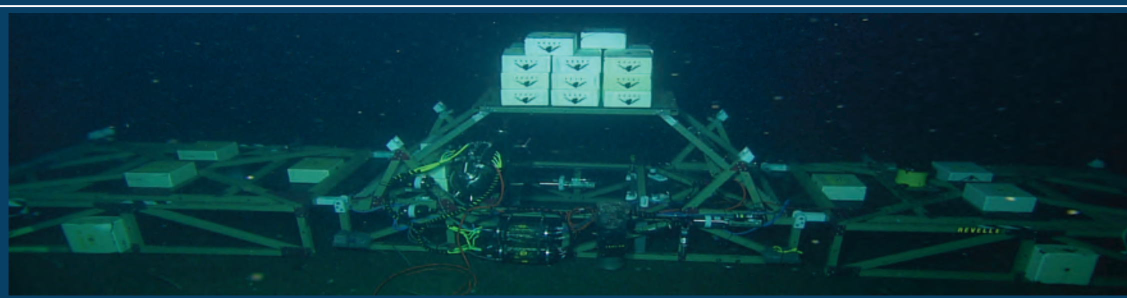
Real Time Control of CO_2 Enrichment Experiments on the Sea Floor Enabled by the MARS Cabled Observatory

Peter G. Brewer, William J. Kirkwood & Edward T. Peltzer

Monterey Bay Aquarium Research Institute Moss Landing, CA 95039

Abstract



Above: The FOCE system deployed on the seafloor near the MARS cabled observatory in Monterey Bay.

We report on the development of Free Ocean CO_2 Enrichment (FOCE) techniques to accomplish realistic (not land-based aquaria) experiments on the response of deep-sea animals to ocean acidification. Similar experiments have long been carried out with ecosystems on land, but the outcome has differed significantly from CO_2 enrichment experiments conducted in enclosed greenhouses.

The equivalent problem in the ocean is far more difficult because of (1) the different physical forcing; (2) the complex reaction rates between CO_2 and seawater; (3) the lack of supporting infrastructure and adequate sensors; and (4) the need for sophisticated and robust control software and hardware. We have overcome almost all of these challenges, and related working systems have already been successfully deployed on the Great Barrier Reef coralline flats with Australian colleagues.

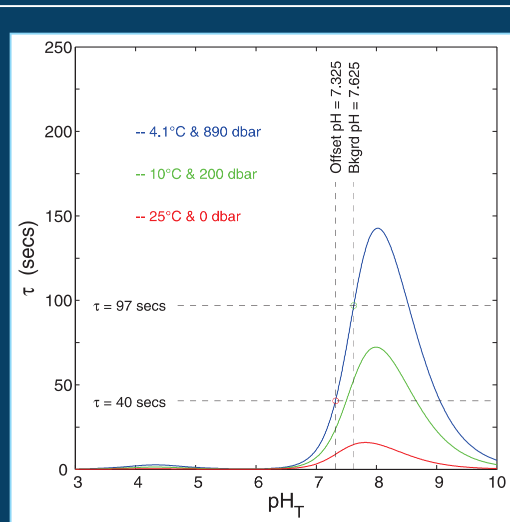
We have used the MARS (Monterey Accelerated Research System) cabled observatory to carry out deep-ocean (880m depth) experiments. The experimental unit is a 1m x 1m x 50cm high chamber with side arms of approximately 3m length to provide the required delay times for the reaction between admixed CO_2 enriched sea water and emergence of the flow into the main chamber. Controllable thrusters maintain a steady flow of seawater through the experiment. We have developed extremely low noise pH sensors that show for the first time the scale and frequency of the tidally driven pH fluctuations in the deep ocean. The software controlling this complex system in real time is robust and a graphical user interface allows the operator remote control of the system over the internet.

Physical & Chemical Control

We use the MBARI/NSF MARS cable for power and experimental control; the system node is at 880m depth, just below the local O_2 minimum. Our basic structure is a flume system with a central box of 1m x 1m x 50cm size in which animals can be placed for exposure to CO_2 rich or O_2 depleted water for experimental purposes. The system is enclosed on two sides and the top to contain the flow of CO_2-enriched sea water. A trap door allows access to the central box.

Critical features of the design are the requirement for flow control, and for providing a time delay between the point of introduction of CO_2-enriched water and access to the controlled experimental chamber.

The primary sensing elements are a set of novel high precision pH electrodes specifically modified for deep-sea work. These provide the primary control for feedback to the CO_2 delivery system so as to maintain a nearly constant pH offset between the external sea water and the controlled volume. The problem is made challenging by the complex and slow kinetics of the CO_2-H_2O reaction which has a strong pH and temperature dependence Under the conditions at our site (depth = 880m, pH = 7.62, T= 4.1°C, S = 34.4) the time required for ~95% equilibrium is ~ 2 minutes.



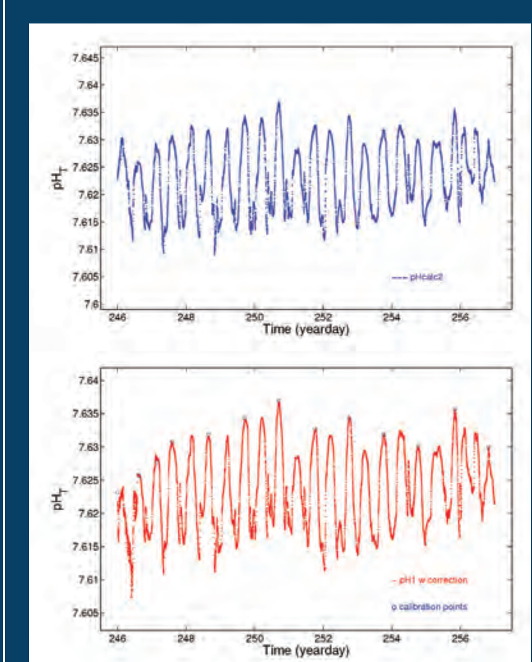
In the figure at above, we see the impact of the slow reaction kinetics of the CO_2-H_2O reaction upon the time required to achieve chemical equilibrium. At background pH, the e-folding time (τ) is ~97 seconds while at the reduced pH from the addition of CO_2-enriched seawater, the e-folding time is 40 seconds. 3τ is needed for 95% equilibrium.

Hardware

Power and communications for the FOCE experiment are supplied by the MARS node via a 30 meter tether. FOCE primarily operates between 200-300W with a maximum power capability of 1 kW. A titanium pressure case (left) allows operation of the electronics at one atmosphere and the large goose neck connector array on top provides 14 water-tight connections for power and communication with the various instruments, modules and sensors. Lower DC operational voltages are generated by an internal power system and are continually monitored via the FOCE GUI on shore. The Ethernet connection is internally routed to a switch which distributes communications among its various components including the main PC104 computer stack, a quad video server, a quad serial server, and a USB server. In addition, the hard-wired Ethernet connection allows for continual data transmission back to shore and remote operator control of the instrumentation.

FOCE's external frame is outfitted with a variety of instruments for both science and engineering monitoring including six pH sensors, two CTDs, a velocimeter, an ADCP, three cameras and lights, a SAMI pCO_2 sensor, and two motor+controller combinations. All instrumentation is wired to the main electronics housing through two oil-filled junction boxes. In addition, FOCE has a variety of internal health monitoring sensors comprised of four humidity sensors, eight temperature sensors, a pressure sensor, and two water detection probes. An external CO_2 subsystem connects to FOCE via an attached underwater mateable connector providing the subsystem with DC power and Ethernet communications. The CO_2 subsystem power can be switched via high voltage safety relay controls on the GUI during CO_2 delivery experiments. Current speeds within FOCE are modulated by two sets of motor-driven fan blades.

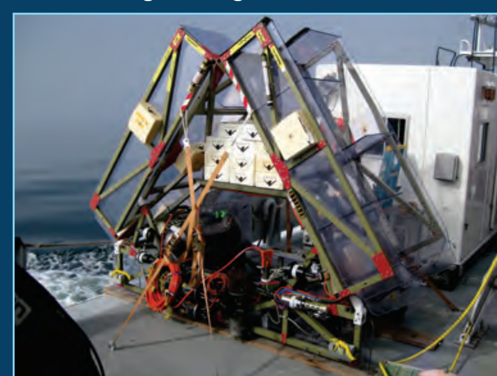
pH Sensors



During the 2009 deployment of FOCE we acquired a very high resolution CTD data set. Since FOCE sits on the continental slope of Monterey Bay, tidal flow drives water from above and below past the experimental site. Using the CTD data we can calculate sigma theta for these water masses and use this to interpolate the other water mass properties from a nearby WOCE station. In much the same way as one would interpolate data between rosette bottles to yield a vertical profile, we can obtain a time series for total alkalinity, total carbon dioxide, phosphate and silicate that can be used to calculate what the background pH should look like during this time period. From this time series record, a semidiurnal pattern emerges that shows both the frequency and the range of pH variations (20 to 25 milli-pH) that we can expect at the FOCE/MARS site. (See blue plot at left.) From this pattern, we then set the specifications for how the pH sensors need to perform in order to measure the natural variation of pH at this site as this is necessary in the implementation of high precision control of CO_2 in seawater using pH for feedback

At left we see the corrected pH signal from one of the four pH sensors in FOCE when only background seawater is flowing through the flume. The semi-diurnal variation driven by the tidal processes is clearly evident, as well as the full range of the predicted pH variation. The calculated background pH signal is not shown as the two plots would directly overlay each other. Calibration points at 12 hour (initially) and 24 hour (long term) are marked by the blue circles.

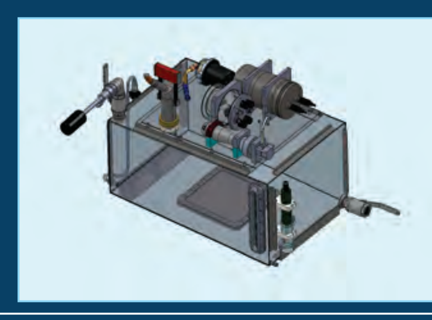
Engineering Tests



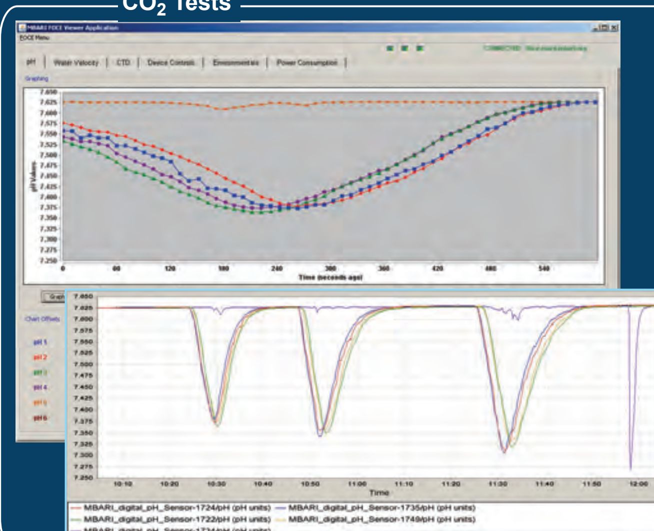
Above: FOCE (with folded chambers) onboard the *R/V Pt. Lobos* prior to deployment.

For the engineering endurance test our goal was for FOCE to run six months continuously without any major hardware or software failures. FOCE was initially deployed on April 26th. While the deployment went well and everything worked upon startup, a leak in the pressure case for pH sensor #6 shorted the 12 V power supply and blew the fuse leaving all 6 pH sensors without power within one hour of deployment. While all of the other instruments were working well, no CO_2 testing was possible. We ran the fans and other hardware through a series of power tests until May 24th when the FOCE flume was recovered. On June 3rd, just ten days after recovering, we redeployed the FOCE frame with a modified power supply for the pH sensors. In addition to the main fuse and isolation relays, each sensor was now individually fused. Oddly enough, even though a different pH sensor body was used, the housing on pH #6 again leaked partially flooding the housing and causing erratic readings. As soon as this was seen, we successfully isolated this sensor from the power supply and proceeded with the experiment using just 5 pH sensors. Since pH sensors 5 & 6 are redundant, we could proceed without any loss of functionality.

The CO_2 delivery system was designed to enable the reliable and accurate delivery of acidified seawater to the inlets of the FOCE flume. The system is comprised of multiple components to permit filling, containment and delivery of CO_2-enriched seawater. Monitoring pH values and electronic feedback controls are integral to this process. The containment enclosure is fabricated from 316 stainless steel and has an interior volume of 248 liters. CO_2 enrichment occurs by simple diffusion between the overlying liquid CO_2 pool (200L when first filled) and seawater flowing through the bottom half of the box. When the seawater absorbs CO_2, its density increases sufficiently that a dense layer of CO_2-enriched seawater forms and this flows from the box when the peristaltic pump is commanded from the FOCE GUI.



CO_2 Tests



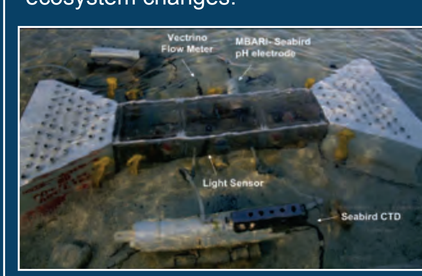
Immediately after installing the FOCE flume on the seafloor, several small injections of CO_2-enriched seawater were made. Each injection (shown in the figures at left) consisted of 4-5 L of surface seawater saturated at one atmosphere with pure CO_2 yielding a working fluid with a TCO_2 of about 50 mM. With each of the three injections a slower flow was used causing a greater pH reduction and a longer residence time for each pulse to pass through the flume. The time lag between the pH sensors on the entrance and exit sides of the experimental chamber is clearly visible. After these three injections were made a final injection was made in the immediate vicinity of the external pH sensor to verify its responsiveness. While these tests were not meant to be quantitative, they did verify that the flume was responding as anticipated and all systems were working well.

Outreach

We are currently developing plans for a basic system for the execution of long-term controlled FOCE experiments at shallow locations in the ocean. We are cooperating with a group from the Stanford Center for Ocean Solutions for experiments to be conducted at a Hopkins Marine Station Site.

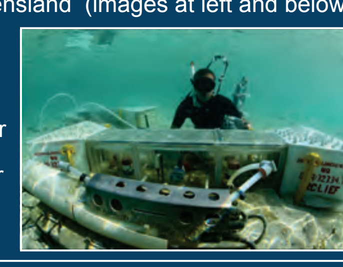
The essential sub-elements are:

(1) a shore-based CO_2 dissolution system to create a working fluid for delivery to the experiment; (2) a mixing chamber where the working fluid is mixed with ambient sea water to create the desired TCO_2 change; (3) a delay loop to allow time for equilibrium to be achieved and the pH signal to be developed; (4) flooding of the experimental zone with the CO_2-enriched water and pH feedback of the signal to the control system; and (5) observation of the induced geochemical and ecosystem changes.



FOCE on the Great Barrier Reef - University of Queensland:

Increasing levels of atmospheric CO_2 present a threat to coral reefs global basis. In December 2009 a shallow water reef version of FOCE called the Coral Proto - Free Ocean Carbon Dioxide Enrichment (CP - FOCE) system was designed and built jointly with the University of Queensland (images at left and below).



The CP-FOCE system has proven to be an important new system for studying the impact of ocean acidification in coral reef environments. CP-FOCE is successfully studying the impacts of the changing water chemistry on the physiology of calcareous reef organisms including corals and calcareous algae. The second generation systems are in place and performing a year long experiment.

Acknowledgments:

We would like to thank the David and Lucile Packard Foundation for continued financial support and the pilots of the *ROV Ventana* and the crew of the *R/V Point Lobos* for their support in the field.